DONOR SOLVENT CHEMISTRY IN LIGNITE LIQUEFACTION

by

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INTRODUCTION

Coal liquefaction by donor solvent processes (DSP) has been studied over the years by many people throughout the world.[1-6] However, lignite liquefaction by DSP was less intensively studied. We were interested in determining how the properties of donor solvents related to lignite liquefaction, particularly with lignites and under low pressure liquefaction conditions.

Our approach was to synthesize a series of donor solvents with different properties by catalytically hydrotreating anthracene oil under various conditions. These solvents were tested for lignite liquefaction under a standard set of conditions. The liquefaction conditions we used were similar to those used by the National Coal Board in their Liquid Solvent Extraction (LSE) process.[7,8] The criteria used for determining the effectiveness of the donor solvents were lignite conversion and filtrate to filter cake ratio. We have tried to correlate these two criteria with the properties of the donor solvent. These properties include total hydrogen content, aromatic content, donatable hydrogen, and molecular weight of the solvent.

We also have studied the effects of other reaction parameters, such as solvent to lignite ratio and the difference between the nominal and real solvent to lignite ratio.

EXPERIMENTAL

A. Chemicals

Anthracene oil was purchased from Crowley Chemical Co. The pure grade tetralin was commercially available from Fischer Scientific. The two lignites used in these experiments were from the Gulf Coast, and their properties are given in Table 1.

B. Apparatus

The reactors used for the solvent/coal ratio studies are better known as "Tubing Bomb" reactors. They were made of 316 stainless steel tubing (3/4" OD, 0.63" ID, 5" long). Both ends were closed with Swagelok caps. A tee was welded at the center of the reactor to accommodate the gas charge port, valve, and pressure transducer. The design is shown in Figure 1. The reactor volume is roughly 23 ml (and has a maximum working pressure of 4400 psig at 538°C).

The reactor used for the solvent quality studies was a 1-liter Magnedrive autoclave from Autoclave Engineers, Inc.

The hydrotreating unit for preparing anthracene oil donor solvents is a continuous feed unit. It has a 300 cc trickle bed reactor. The reactor is filled first with 100 cc of inerts (ceramic beads), then 100 cc 1/16" extrudates $Ni-Mo/Al_2O_3$ catalyst from United Catalysts, and finally the remaining 100 cc with inerts again. The arrangement is shown in Figure 2.

C. Experimental Procedure

Experiments for solvent quality studies were carried out with a 1-liter autoclave. For the solvent to lignite ratio studies, the tubing bomb reactors were used.

For a typical solvent quality study experiment, 300 g of hydrotreated anthracene oil and 200 g of lignite A (dried, 40 mesh-) were placed in the reactor. The reactor was pressure tested for leaks at 1000 psig with nitrogen. The nitrogen gas was released to atmospheric pressure before starting the heating.

While stirring at 1000 rpm, the reactor was heated slowly (about 90 minutes) to 400^oC and was kept at this temperature for one hour. The maximum pressure for these runs was about 600-800 psig. After reaction, the reactor was cooled quickly with cold water (the reactor is equipped with an internal cooling coil). The reaction mixture (liquid and solid) was transferred and filtered through a 15 cm diameter Whitman #4 paper filter. The filter funnel was heated with steam during filtration. The filtration was stopped when there was no obvious liquid left in the filter funnel. The filter cake was then mixed with 300 ml of quinoline. The mixture was stirred for 30 minutes and then filtered as above, except no steam was used. The filter cake was washed with 100 ml of quinoline and then it (the quinoline insolubles) was dried overnight in a vacuum oven at 110^oC. The quinoline conversion was calculated as shown below:

Quinoline Conversion % = 100% - % quinoline insoluble (ash free)

The quinoline conversion includes the gas yield.

For the solvent ratio studies, 2 grams of dried 40 mesh-lignite B was placed in the tubing bomb along with the appropriate amount of tetralin (2, 4, 6, or 8 grams). For the reactor loading studies, the solvent to lignite ratio was constant at 2, but the total amount of the mixture varied (5.5, 6.6, 8.8, and 12.1 grams).

For each test, the experiment was duplicated. The results reported are averaged values. For a typical run with tubing bomb reactors, 4 reactors were secured on a rack which was then lowered into the preheated (410^oC) fluidized sand bath. After shaking the reactor at 180 rpm for one hour, the reactors were lifted from the sand bath and quickly quenched with cold water. The reactors were then depressurized. The gas mixture was not analyzed. The reaction mixture (liquid and solid) was diluted with 50 ml of cyclohexane and stirred for 30 minutes. The mixture was then filtered with a medium

fritted glass funnel. The filter cake was washed with 20 ml of cyclohexane and then was dried overnight in a vacuum oven at 110°C. The cyclohexane insoluble filter cake was used to calculate the cyclohexane conversion, as was done for the quinoline conversion.

For tetrahydrofuran (THF) conversions, the cyclohexane insoluble was further mixed with 50 ml of tetrahydrofuran, stirred, filtered, washed, and dried in the same manner as described above. The THF conversions were calculated similarly. Again, all these conversions (quinoline, cyclohexane, and THF) include the gas yields.

The donatable and aromatic hydrogens were measured by proton NMR.

RESULTS AND DISCUSSION

A total of 15 donor solvents were synthesized by catalytic hydrotreating of anthracene oil at various conditions. Their properties are listed in Table 2. These solvents were tested as lignite liquefaction solvents under low pressure with no added molecular hydrogen during liquefaction. The reaction pressure varied from 600-800 psig because of the difference in vapor pressure of the solvents at reaction temperature. The unhydrotreated (raw) anthracene oil was also used for comparison purposes. We analyzed our results in relation to the individual properties of the solvent, such as total hydrogen content, aromatic hydrogen content, donatable hydrogen, and average molecular weight. In reality, probably each of the above properties contributes to a different degree in each solvent. This may explain some of the scatter in the data. The results and discussions will be grouped under the solvent properties mentioned above. We will also discuss the difference between the real and nominal solvent to lignite ratio effect in lignite liquefaction.

A. Effect of Total Hydrogen Content

We tried to correlate the total hydrogen content of the sixteen solvents (15 prepared from hydrotreating anthracene oil and one from the raw anthracene oil) with the lignite liquefaction conversions (quinoline conversions). The results are shown in Figure 3. The lowest conversion (71%) is associated with lowest total hydrogen content of 6.5%. As the total hydrogen is increased slightly to 7.22%, the conversion improves significantly from 71 to 89%. With further increases in total hydrogen content, the conversion only increases slightly and levels off at about 98%, when the total hydrogen content is about 8-9%. When the total hydrogen is again increased further to the neighborhood of 10%, the conversions decrease to the low 90's. The optimum total hydrogen seems to be in the area of 8 to 9%.

B. Effect of Aromatic Hydrogen

The lignite liquefaction conversion (quinoline) is plotted versus the aromatic hydrogen content (Figure 4). The effect of aromatic hydrogen on lignite liquefaction conversion is very similar to that of total hydrogen content. The low conversions are found on the two extreme ends of the aromatic hydrogen content scale. For example, the low conversions of 71 and 91% are found with the highest

aromatic hydrogen content of 4.6% and the lowest aromatic content of 1.85%, respectively. The maximum conversion is located in the middle of the aromatic hydrogen content scale (about 3%). In other words, a good process solvent shouldn't be either too saturated or too aromatic.

C. Effect of Donatable Hydrogen

The general definition of donatable hydrogen is that hydrogen of any molecule that can be donated to the coal molecules or radicals during liquefaction reactions. We have tried to find quantitatively how much of this type of hydrogen in the solvent is necessary for high conversion. We tried to determine the value of potentially donatable hydrogen (hydrogen α to the aromatic ring) by proton NMR. The values are expressed in terms of absolute weight percent of the hydrogen in the solvent that are potentially donatable. These reported values may not be the same amount of actual donatable hydrogen that is required or consumed during liquefaction reactions. The donatable hydrogen from our solvents ranges from 1.43 to 2.76 wt %. These values are plotted against their corresponding conversion values (Figure 5). The raw anthracene oil has a very small amount of donatable hydrogen (1.43 wt %) and, as expected , gives a correspondingly low conversion value of 71%. Overall, the conversion values seem to increase with the increase in the amount of donatable hydrogen. There is no maximum point found in this curve as was found with the other two (total and aromatic hydrogen curves, Figures 3 and 4). In other words, over the range studied there is no limit; the more, the better.

D. Effect of Total Hydrogen on Filtrate Yield

A liquefaction process may include filtration as a solid/ liquid separation step. We were interested to see if the solvent properties that enhance high conversion also enhance high yield of filtrate. It is possible that a good donor solvent may not be a good solvent for dissolving liquefied lignite products. High yield of filtrate may be just as important as high quinoline or cyclohexane conversions, because in a commercial process the use of an extraction solvent, such as quinoline, would be prohibitively expensive.

The reaction mixture, after having cooled to ambient temperature, was filtered. The weight ratio of the filtrate to the filter cake is plotted against the total hydrogen content of the solvent (Figure 6). This plot produces a curve which is similar to that of conversion vs total hydrogen. The maximum occurs at 8 to 9% of total hydrogen content. The maximum quinoline conversions also occur in this region. This suggests that the best donor solvent produces the highest conversion and also produces the highest filtrate to filter cake weight ratio, or the highest liquid product yield.

E. Effect of Molecular Weight

The average molecular weight of the 16 solvents studied ranges from 160 to 260. The conversion data are somewhat scattered (Table 2). However, the solvents that have high conversions (97%+) seem to have a higher molecular weight (200+). On the other hand, the

solvents with low conversion seem to associate with lower molecular weights. The reason for this will be explained in our solvent to lignite ratio studies.

F. Effect of Solvent to Lignite Ratio

For the study of solvent to coal ratio effect, we used THF and cyclohexane conversions. For example, THF conversion is the yield of gases and THF soluble lignite products. The results are illustrated in Figures 7 and 8. The data suggest that there is a difference between nominal and real solvent to lignite ratio. The nominal ratio is defined as the weight of the solvent divided by the weight of lignite charged to the reactor. The real ratio is defined as the calculated weight of the solvent in the liquid state at reaction temperature divided by the weight of the lignite charged into the reactor. The real ratio is considerably smaller than the nominal ratio because a considerable amount of the solvent is vaporized at reaction temperature of 410°C.

The conversion results (cyclohexane) are plotted against the nominal weight ratio (open triangle) and real weight ratio (filled squares). The difference is that the conversion won't start leveling off until after 3/1 for the nominal and 1.5/1 for the real ratio. Thus, for the higher molecular weight solvent, less starting solvent is needed for the equivalent conversion.

The experiment with nominal solvent to lignite ratio of 2/1 was repeated with 1000 psig of hydrogen in one run and nitrogen in the other. The conversion (cyclohexane) is increased from 33% (nominal ratio) to 62%, and there is no difference in conversion found between the run with hydrogen and nitrogen. This suggests that the difference in conversion is due to the pressure effect. That is, the presence of the high pressure of hydrogen or nitrogen suppresses the vaporization of the solvent. Thus, it is the liquid solvent that is important for promoting high conversion.

The fact that the solvent has to be in a liquid state for optimum conversion is again demonstrated in another set of experiments. In this series of experiments, the solvent to lignite ratio is held constant at 2. The percent of the reactor volume being filled with the solvent and lignite mixture varied from 25, 30, 40, and 55 volume %. The conversions, both cyclohexane and THF, are plotted against the volume % of reactor filled with slurry as shown in Figure 8. The conversion results show that the conversion increases dramatically with the increase in the reactor volume usage of 30 to 40%. From 40 to 50% only a slight increase is found. This means the difference between nominal and real solvent (tetralin) to lignite ratio is small once the reactor is more than 40% full.

To sum up, from our solvent property studies, the ideal solvent should not be too aromatic or too saturated. The presence of an aromatic group and saturated group in the same solvent molecule (such as hydroaromatics) is necessary to provide a source of donatable hydrogen. For our particular solvent system (derived from anthracene oil), the optimum solvent should have about 3% aromatic hydrogen, a total hydrogen content of 8 to 9%, some donatable hydrogen (2.5%), and

a high boiling range. From our solvent ratio studies, a solvent in a liquid phase is important for promoting high liquefaction conversion, and the solvent to lignite ratio should be in the neighborhood of 2 for high conversion.

CONCLUSIONS

The results from solvent property correlation studies suggest that the optimum lignite liquefaction solvent should have the following characteristics:

1. Some aromatic groups (3% aromatic hydrogen content),

2. Total hydrogen content of 8-9%,

3. Some donatable hydrogen (2.5%),

4. And a high boiling point range (preferably 500-1000°F).

The results from solvent to lignite ratio studies have suggested that only the solvent in the liquid phase is important for promoting high conversion in these high temperature reactions. The optimum solvent to lignite ratio is in the neighborhood of 2. These requirements for high liquefaction conversion are probably more demanding for our system than any other processes because all the required hydrogen for stabilizing the lignite liquefaction products come from the starting solvent. We don't add molecular hydrogen to our system; thus, hydrogen shuttling through the solvent system is insignificant.

References

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Table 1

Lignite Characteristics

	Gulf Coast Lignite	
	_A_	_B_
Moisture (%) Ash Received	31.69	22.4
Proximate, %, Dry Basis		
Ash	15.77	11.5
Volatiles	54.69	45.
Fixed Carbon	29.54	44.
Ultimate, %, Dry Basis		
Carbon	59.21	64.3
Hydrogen	5.53	4.5
Nitrogen	0.55	1.2
Sulfur	_2.91_	_1.2_
Ash	15.77	11.5
Oxygen	16.03	17.4
_H/C_	_1.12_	0.84
Btu/lb, Dry Basis (calc.)	10988	10964

Table 2

Donor Solvent Characteristics

Solvent No.	Solvent Characteristics[1]				Conversions (%)[2]
	$H_t(\%)$	$H_a(\%)$	$H_d(\%)$	Mwt	
1*	6.5	4.6	1.43	173	71
2	7.22	4.08	1.92	174	89
3	10.26	1.85	2.05	157	91
4	7.13	2.85	2.35	157	92
5	9.84	2.36	2.46	169	92
6	9.9	2.28	2.38	166	93
7	7.84	2.63	2.43	181	94
8	9.99	2.20	2.20	164	94
9	9.95	2.19	2.49	168	95
10	9.9	2.19	2.39	166	95
11	8.19	2.67	2.46	169	96
12	10.08	2.12	2.32	166	96
13	9.05	2.79	2.43	196	97
14	8.35	2.72	2.34	252	98
15	8.11	3.08	2.43	204	98
16	8.93	2.98	2.76	260	98

[1]H_t, total hydrogen content; H_a, aromatic hydrogen; H_d, donatable hydrogen determined by proton NMR.

[2]Conversion is the sum of gas yield and quinoline soluble, on maf basis.
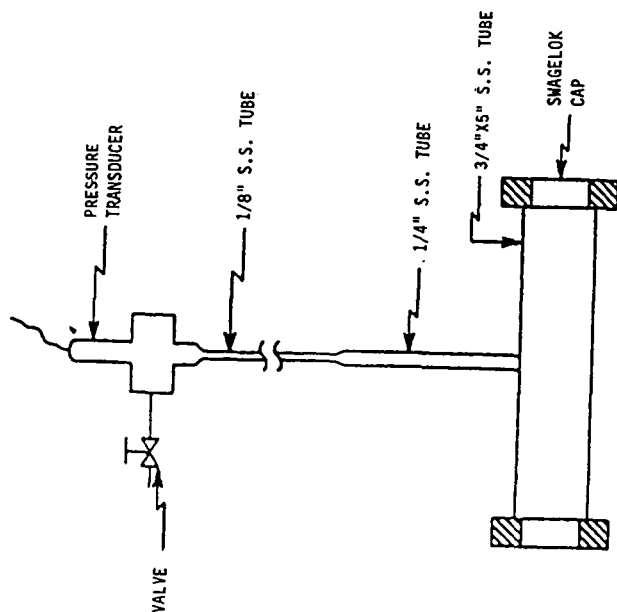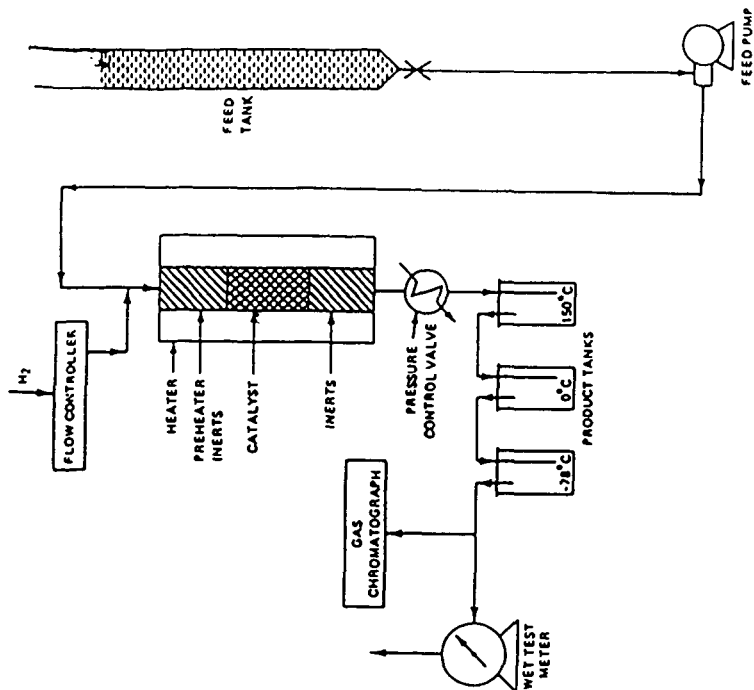
*Raw anthracene oil.

Figure 2
SUPERCRITICAL HYDROTREATING SYSTEM

FEED TANK

FEED PUMP

FLOW CONTROLLER
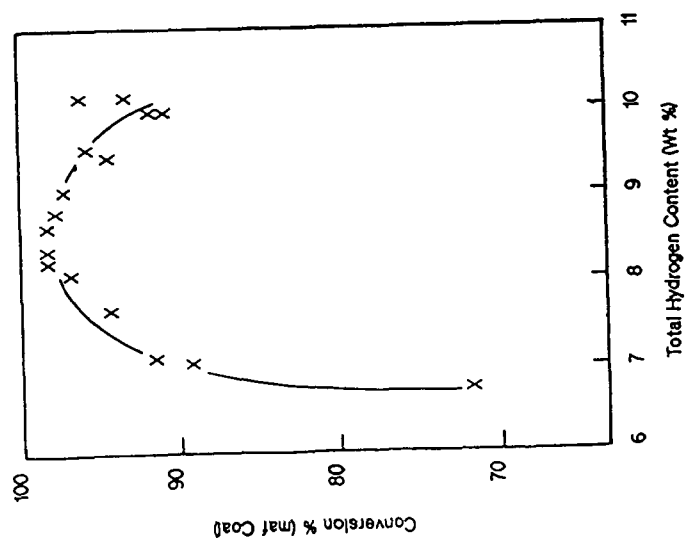
H₂

HEATER
PREHEATER
INERTS
CATALYST
INERTS

PRESSURE
CONTROL VALVE

GAS
CHROMATOGRAPH

PRODUCT TANKS

150°C   0°C   -78°C

WET TEST
METER

PRESSURE
TRANSDUCER

1/8" S.S. TUBE

.1/4" S.S. TUBE
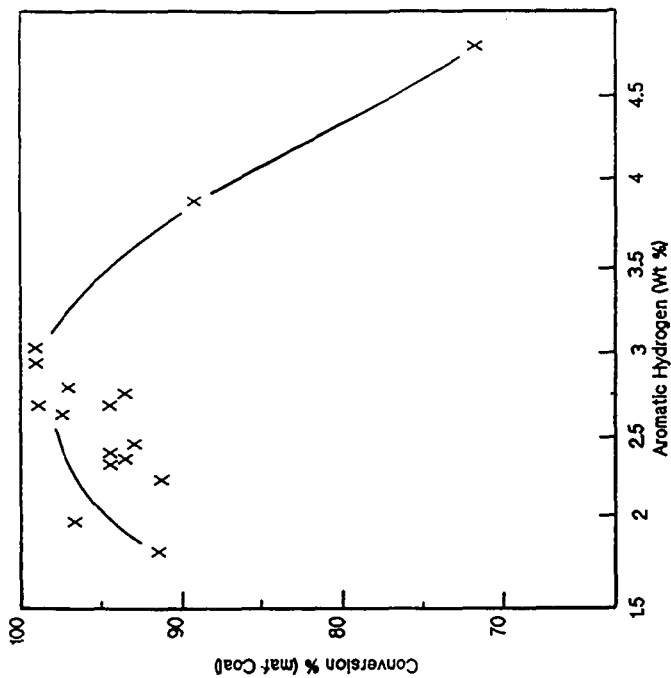
3/4"X5" S.S. TUBE

SWAGELOK
CAP

VALVE

FIGURE 1
TUBING BOMB REACTOR

398

FIGURE 4. EFFECT OF AROMATIC HYDROGEN ON CONVERSION

FIGURE 3. EFFECT OF TOTOL HYDROGEN ON CONVERSION
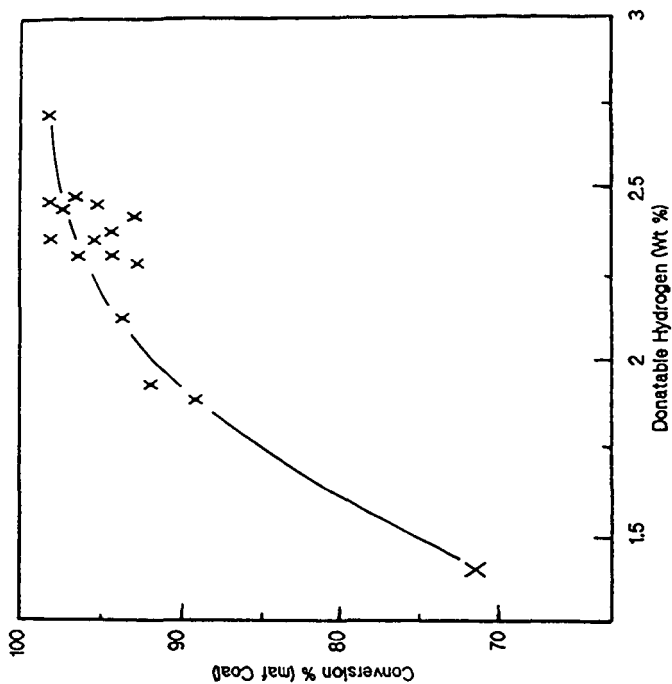
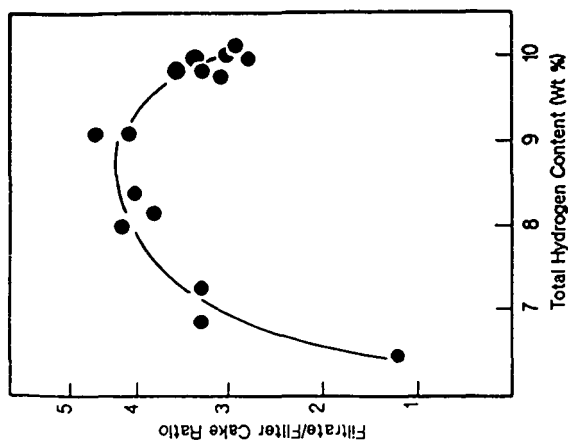FIGURE 5. EFFECT OF DONATABLE HYDROGEN ON CONVERSION
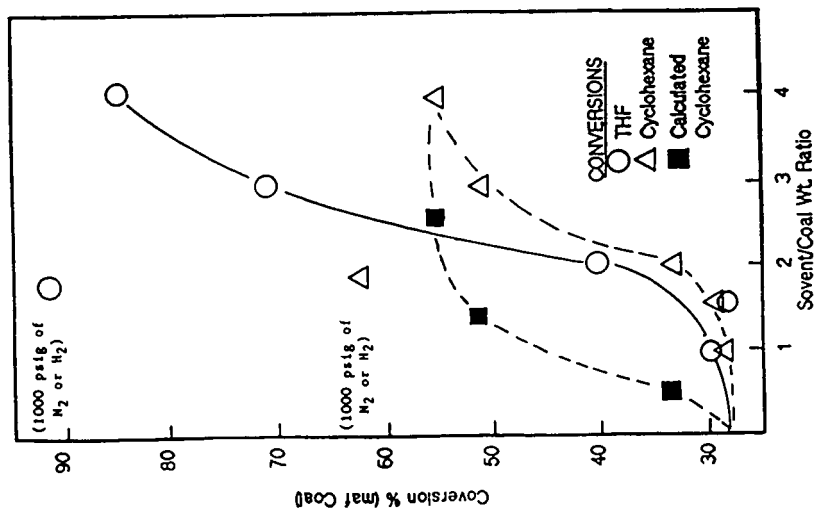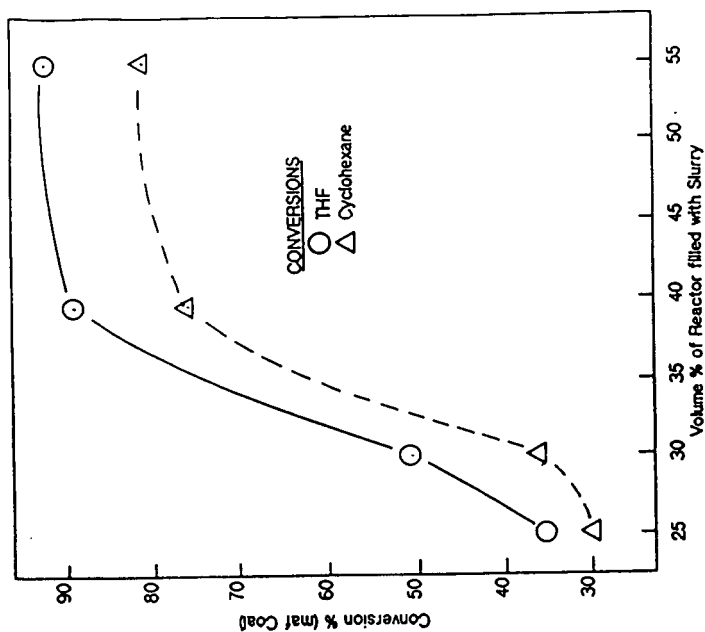

FIGURE 6. EFFECT OF TOTAL HYDROGEN ON FILTRATE YIELD

400

FIGURE 8. REACTOR LOADING EFFECT
(Lignite B, 410 C,S/C = 2, 1 hour)

CONVERSIONS
○ THF
△ Cyclohexane

FIGURE 7. SOLVENT TO COAL RATIO EFFECT
(2 g Lignite B, Tetralin, 410 C, 1 hour)

CONVERSIONS
○ THF
△ Cyclohexane
■ Calculated
  Cyclohexane

401